Magnetoelectric nano-$Fe_3O_4/CoFe_2O_4$‖$PbZr_{0.53}Ti_{0.47}O_3$ composite

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A new magnetoelectric hybrid device composed of a nanoparticulate magnetostrictive iron oxide-cobalt ferrite film on a piezoelectric lead zirconic titanate crystal serving as both substrate and straining medium is described. Nano-$Fe_3O_4/CoFe_2O_4$ particles, ranging from 5 to 42 nm, were prepared using a variation of the sol-gel method. A small electric field, 5–10 kV cm^{-1}, applied at the coercive field of the nano-$Fe_3O_4/CoFe_2O_4$ component modulates the film magnetization up to 10% of the saturation magnetization of ferrite. At the smallest particle size of 5 nm, the coercive field is as low as 25 Oe and the inverse ME_E voltage coefficient is as high as $(10.1\ V/cm\ Oe)^{-1}$. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2841064]

The recent surge of papers describing magnetoelectric composites (MECs) may be divided into two groups; the first consisting of papers reporting on metal-oxide composites and the second containing those publications dealing with oxide-oxide structures. High MEC susceptibilities at low magnetic fields are achieved with metal-oxide MECs by choosing either glassy metals or designing highly magnetostrictive metallic components with zero demagnetization factor.[1,2] Similar approaches are not as readily accessible for oxide/oxide ME composites as these are predominantly fabricated by thin film technologies, e.g.,[3] and the oxide featuring the highest magnetostriction, $CoFe_2O_4$ (CFO), possesses a large magnetocrystalline anisotropy. The fully epitaxial self-assembled 3-1 CFO/$BaTiO_3$ ME composites[4] represent somewhat of an exception. Therefore, in an effort to reduce the effective magnetocrystalline anisotropy and thereby the coercive force of CFO, we developed a nano-$Fe_3O_4/CoFe_2O_4$‖lead zirconic titanate (PZT) MEC, whose fabrication and properties are described in the following.

To achieve a highly effective magnetoelectric signal, ME composites require high piezoelectric and magnetic susceptibilities.[5,6] $Pb(Zr_{0.53}Ti_{0.47})O_3$ is a well-understood piezoelectric material fulfilling this requirement. Ferromagnetic bulk Co ferrite is a good choice due to its high magnetostriction. However, because of its high magnetocrystalline anisotropy,[7] it has a low magnetostrictive initial susceptibility that results in a low magnetoelectric susceptibility $d\lambda/dH$. In nanoparticles, the effective magnetocrystalline anisotropy is lowered and $d\lambda/dH$ can be increased while maintaining its high saturation[8] as has also been demonstrated for Co ferrite.[9] Therefore, in order to create an all-oxide MEC with a large ME coupling coefficient, a nano-$Fe_3O_4/CoFe_2O_4/Pb(Zr_{0.53}Ti_{0.47})O_3$ was developed. This composite yields giant ME voltages under significantly lower magnetic bias fields than previously reported for CFO/PZT MECs.[10] Its manufacture and properties will be described next.

The composite was manufactured by spinning a CFO sol-gel[11] onto a mirror polished PZT single crystal substrate, obtained from Fuji Ceramics, Inc. The deposition technique and substrate were chosen to obtain lower sintering temperatures and good homogeneity of the film as well as proper stress transfer between the components of the composite by avoiding large surface roughness. The sol solution of $CoFe_2O_4$ with a molar ratio of $Co^{2+}:Fe^{3+}=1:2$ was repeatedly spin coated onto the PZT substrate until a smooth precursor film was obtained.[12] Subsequently, the composite was annealed for 15 min at different temperatures, 450–650 °C, to obtain different nanosizes and compositions between Fe_3O_4 and $CoFe_2O_4$. The final composite consisted of a 5 μm thick film of nano-$CoFe_2O_4$ on 100 μm PZT. Special attention was given to heat treatment at compositions intermediate between Fe_3O_4 and $CoFe_2O_4$ as Bickford *et al.* have shown that addition of only a small amount of magnetite to cobalt ferrite changes the sign of the anisotropy constant from negative to positive.[13] Our experiments extend this idea to the additions to cobalt ferrite.

The structure of the composites was characterized using scanning x-ray microdiffraction (D8 DISCOVER with General Area Diffraction Detector System for combinatorial screening by Bruker-AXS). x-ray diffraction (XRD) shows the typical signature of the composite: two sets of well-defined peaks are observed belonging to PZT and $CoFe_2O_4$. No additional or intermediate phase peaks can be identified. The minor constituent Fe_3O_4 (see below) was not specifically identified as its XRD signature is almost identical to that of CFO. The broad CFO XRD peaks are indicative of nanoparticle formation. The morphology and cross-section examination of the film was made using an environmental scanning electron microscope and an atomic force microscopy. A well-bonded interface was discerned.

Magnetic properties of the nano-CFO films were measured using a superconducting quantum interference device. We measured the field dependent magnetization at room temperature by applying magnetic fields parallel to the plane of the film. The magnetic hysteresis loops of the films demonstrate the effect of the different annealing temperatures (450–700 °C) on the coercivity as well as saturation magnetization. It was observed that the value of the coercive field gradually decreases with decreasing annealing temperature (Fig. 1), as expected. At an annealing temperature of 450 °C, the coercivity is $H_c \approx 25$ Oe. The saturation magnetizations of in-plane loops yielded 375 emu/cm^3 independent of the particle size. The temperature dependence of the saturation magnetization of a 22 nm-CFO film yields Curie tempera-

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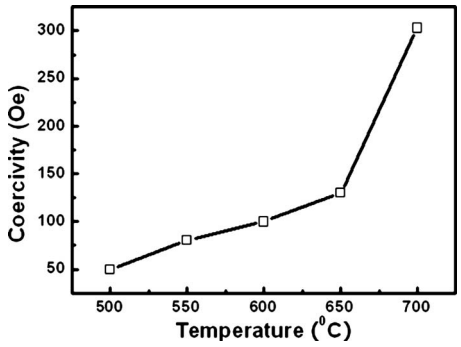

FIG. 1. The coercivity field, determined at room temperature, of the nano-$Fe_3O_4/CoFe_2O_4$ component of the MEC as a function of the annealing temperature.

tures of 700 and 860 K, indicating that the particles consisted of approximately 91% CFO and 9% Fe_3O_4.

In order to demonstrate the ME coupling of the ferroelectric and ferromagnetic components of the composite, the average in-plane magnetization of the CFO nanoparticles was determined as the PZT substrate was alternately poled.[14,15] The change of magnetization upon the application of an electric field was measured using a vibrating sample magnetometer in the direction of the biasing magnetic field. The MEC was electroded[16] as described before so that an electric field could be applied while the magnetization was determined. Figure 2 displays the variation of the magnetization at the coercive field of 80 Oe as the electric field was sinusoidally varied as a function of time. These data yield a magnetoelectric coefficient $ME_E=10.1$ V/Oe cm, which compares favorably with published values.[17]

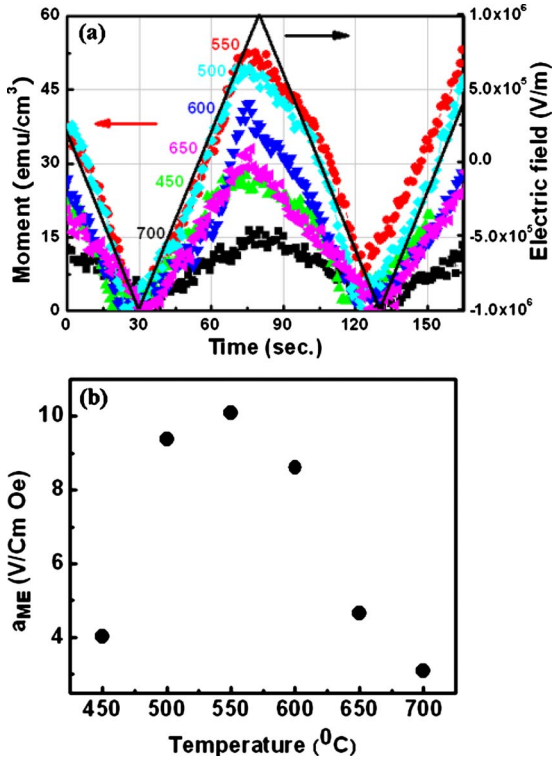

FIG. 2. (Color online) Top: electrically induced magnetic switching, the moment of magnetization dependence of external applying electric field (-10^6-10^6 V/m). bottom: room temperature inverse magnetoelectric susceptibility, $\alpha_{ME}^{-1}=4\pi\Delta M/\Delta E$, of the MEC as a function of the annealing temperature, corresponding to the top figure.

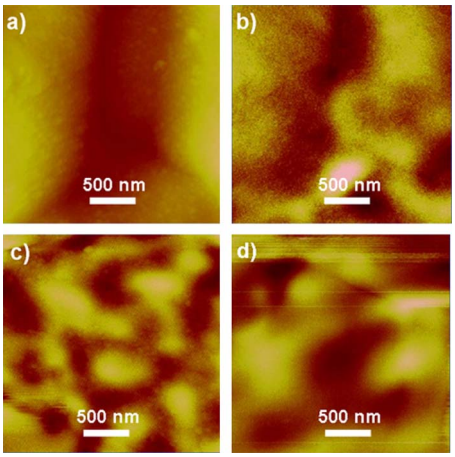

FIG. 3. (Color online) MFM images of nano-$Fe_3O_4/CoFe_2O_4$‖$PbZr_{0.53}Ti_{0.47}O_3$ MECs processed at temperatures of (a) 450 °C, (b) 500 °C, (c) 550 °C, and (d) 600 °C.

If the elastic constants of the composite's components are equal to each other, the inverse magnetoelectric response coefficient of a MEC can be written as

$$\alpha_E = \frac{\partial M}{\partial E} \approx \mu|\lambda|d.$$

For the present composite, the permeability μ is determined by the magnetic characteristics of a CFO/Fe_3O_4 solid solution. At room temperature, it attains a maximum of $\mu_{max}=50$.[18] The magnetostriction λ is equal to that of the CFO/Fe_3O_4 solid solution. It is known that its value is smaller than that of pure CFO. Its maximum value is approximately given by $\lambda\approx-150$ ppm.[19] Finally, the piezoelectric coefficient d of the PZT composition used is given by $d=125$ pC/N.[20] The cited values of the coefficients yield an estimate for the inverse magnetoelectric response coefficient of the present MEC of $\alpha_E\approx9.4\times10^5$ ps/m or $\alpha_E\approx1.7\times10^2$ V/cm Oe. This magnitude is 20 times larger than the maximum experimentally determined value of 10.1 V/Oe cm. It must be remembered, though, that only the portion of the permeability related to magnetization rotation and 90° domain wall motion pertains to this study. Figure 3 showing how the domain structure at maximum coupling differs from the others might be an indication of that fact. However, it appears that the present CFO/magnetite‖PZT MEC magnetoelectric performance can be improved, likely by increasing the permeability of the CFO/Fe_3O_4 solid solution by adjusting the magnetite content. In this work, the magnetite additions were not planned but the result of the simple annealing procedure in air. Figures 1 and 2 (below) indicate that the coercivity and the inverse magnetoelectric coefficient depend on the temperature, likely because the magnetite content of the solid solution varies. It appears that at the annealing temperature of 550 °C, the product of the permeability and the magnetostriction is optimized. At a lower annealing temperature, the magnetite content would be large leading to a large permeability. However, the CFO content would be small and therefore the magnetostriction. The situation is reversed at temperatures higher than the optimum.

In summary, a very simple, inexpensive, double-layer all-oxide nano-Fe_3O_4/CFO‖PZT multiferroic 2-2 composite heterostructure has been prepared and studied. Ferromag-

netic films of nano-$Fe_3O_4/CoFe_2O_4$ were obtained by a spinning a suitable sol-gel onto a $Pb(Zr_{0.53}Ti_{0.47})O_3$ substrate. The double-layer film contains PZT and Fe_3O_4/CFO phases and shows good electric-field-induced magnetoelectric properties. We can obtain a very low coercivity value of magnetostrictive $Fe_3O_4/CoFe_2O_4$ phase, less than 100 Oe through controlled sol-gel and annealing processing. The resulting ME laminates have very large inverse ME voltage coefficients. The bias field obtained in this study can be further reduced and the inverse magnetoelectric response coefficient increased by changing the ratio between the Fe_3O_4 and CFO components by targeted annealing.

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